The Action of Trioxymethylene on Various Hydrocarbons in the Presence Anhydrous Aluminum Chloride

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VAMAN R. KOKATNUR

B.Sc. Bombay University, India, 1912
M.S. University of Minnesota, 1914

A Thesis

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF MINNESOTA
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THEORECTICAL.

EXPERIMENTAL.

ACKNOWLEDGMENT.

This work was begun at the suggestion of Dean G. B. Frankforter, in order to extend the dehydrating action of aluminum chloride, which he first reported at the International Congress of Applied Chemistry at New York City. During the entire work, the author has had many valuable suggestions made to him by Dr. Frankforter, which saved him much unnecessary trouble. The author takes this opportunity of expressing his hearty appreciation for his help and kindness.

INTRODUCTION.

Organic chemistry, when it was so named, was particularly restricted to the study of those compounds that occur in plants and animals and to their decomposition products. At the beginning of the last century, it was generally believed that substances occurring in animal and vegetable kingdom could only be formed by the help of a mysterious energy called vital force. Even after Wöhler in 1828 had synthesized urea, a substance occurring in animal body, this belief held great sway on the minds of chemists of that time. But in the first half of the last century, when Kolbe and Berthelot synthesized acetic acid and fats, this belief in the vital force began to lose its ground in the chemical world.

The theory of vital force has been completely discarded today and thousands of compounds occurring in plant and animal life have already been prepared in the laboratory. Even the possibility of synthesizing proteids is no longer a question of doubt. Among some of the triumphs of organic chemistry the synthesis of camphor, indigo, sugars, rubber and perfumes. may be mentioned.

During the last quarter of a century organic chemistry has grown by leaps and bounds. Hardly a week passes without some new compounds being synthesized in the chemical laboratories of the world. We already know of about one hundred and fifty thousand organic compounds, and yet, we are just on the threshold of this unlimited and unexplored domain. The

number of compounds known to us today seems like a drop in the limitless ocean of new substances yet to follow. It has been shown mathematically by Calay* that the number of isomers of hydrocarbons alone, is simply beyond numbers. He showed that even a simple substance like Tridecane, $C_{13}H_{28}$, may exist in eight hundred and two different isomeric forms. Triacontane, $C_{30}H_{62}$, may exist in millions of different forms, while Hexacontane, $C_{60}H_{122}$, might form isomerides beyond human comprehension. Add to this the innumerable derivatives and substitution products and a fair idea may be formed of the infinite limits of organic chemistry.

Catalysis:

Most of the organic reactions occurring in nature are generally slow. Many of them require days and even weeks. A familiar illustration may be found in the production of starch in plants by what is known as the photosynthesis. The discovery of catalysis has been a great help in accelerating the velocity of both organic and inorganic reactions. It has been of especially vital importance in organic synthesis. Some of the well known condensation reactions such as Baeyer's, Grignard's or Friedel and Crafts' reaction, are based on catalysis.

Catalysis may be defined as a chemical change, either analytic or synthetic, brought about by the mere presence of a substance, which does not permanently enter into the chemical reaction; or as stated by Ostwald, an increase in the reaction velocity beyond the normal, by some substance which does not enter the reaction.

Catalysis is known to the world from almost prehistoric times. This early knowledge, however, is restricted to certain reactions occurring in nature, especially those processes commonly known as fermentations. Pliny gives an interesting description of the fermentation of both wine and vinegar. Hindus of the Vedic age (2000 B. C.—5000 B. C.) seem to have known of fermentation. In Rig Veda, the oldest document of the Aryan race, the drinking of fermented and distilled liquor is forbidden. In works of Nyâya-Vaisheshika school of philosophy, (about sixth century B. C.) a peculiar sort of contact between heterogenous

* Phil. Mag. (4) 47, 444.

atoms is described under the name of dynamic-contact. The description of this resembles so much, our modern conception of both positive and negative catalytic action, that part of it is quoted below. *"When such atoms do not combine under the mere application of heat, they require to be surrounded, excited or energized by atoms of other Bhûta or elements." As an example, water is mentioned as acting catalytically on saps and fruit juices in imparting to them taste, aroma, etc., under the influence of heat. It is distinctly mentioned that any element can act catalytically on other elements. The ideas on negative catalysis are thus described: "The earth element alone is capable of exercising the power of arrest or inhibition of molecular motion or the power of counteracting the tendency in a given set of atoms to fall into a peculiar order or group." These ideas are certainly remarkable when we remember their antiquity. In Europe, catalysis probably was not used in the laboratory until the time of Scheele (born in 1742). But remarkable as it may seem, the Hindus used catalysis in the laboratory earlier than the twelfth century. The Hindu medical works in Sanskrit, mention gold as being used catalytically in the preparation of Swarna-Sindura, red mercuric sulphide, HgS.** This is probably the first record of gold being used to facilitate the formation of HgS.

The Hindu physicians, however, did not try to explain the reaction. In Europe it was probably Libavius (born 1540) who was first attracted by the phenomenon of catalysis. Later Scheele entered the field and definitely demonstrated the phenomenon of catalysis. Berzelius collected all the so-called catalytic reactions and brought them to the attention of the world. He regarded catalysis as an effect of a peculiar electrochemical form of energy. His great pupil Mitscherlich, however, did not agree with his master and tried to explain it by the contact theory, according to which, the catalytic agent was supposed to be in close contact with the reacting substances.†

Liebig tried to explain catalysis by his well known vibratory theory. He believed that the atoms of a substance, due to their

*History of Hindu Chemistry by Dr. P. C. Ray, Vol. II, pages 199-200.
** Dr. P. S. Roy's History of Hindu Chemistry, Vol. II, 136, 155, 156.)
†Pogg. Ann 31, 281.

inherent energy were in constant vibration. On account of this vibration, he thought, the atoms of a body exerted an influence over those of other bodies, thus rearranging their equilibrium. Brodie* explained it by means of "Cyclic actions" and proposed that term for catalysis. Wagner believed that the catalysis took part in the reaction and hence proposed the term "pseudo catalysis." Playfair** later repeated Liebig's experiments with the view of explaining them on purely mechanical grounds. He explained the phenomenon of catalysis on the basis of cohesion. Mercer† was the first to make a distinctly catalytic experiment. He explained catalysis as a result of the chemical affinity of the catalyst with the reacting substances. He was the first to use copper, tin, manganese and other metals as catalysts.

In spite of the work of such savants as the ones mentioned, our knowledge of catalysis is yet very unsatisfactory. It would not be too much to say that we are almost as much at sea today, as we were yesterday, regarding the true cause of catalysis. However, the most widely accepted explanation of catalysis is, that the catalyst and one of the reacting substances form a temporary combination, which is immediately broken down. The preparation of oxygen by Brin's process, or by the method of potassium chlorate, are familiar examples of catalysis. In the first case barium oxide acts as a catalyst. At about seven hundred degrees it forms an intermediate compound, barium peroxide, which immediately breaks down, giving off oxygen, according to the following simple equation:

$$BaO + O = BaO_2$$

In the second process for the preparation of oxygen potassium per manganate is formed from manganese dioxide as an intermediate compound, which immediately breaks down to potassium chloride and maganese dioxide as follows:

$$2\ KClO_3 + 2MnO_2 = 2KMnO_4 + Cl_2 + O_2$$
$$2\ KMnO_4 + Cl_2 = 2KCl + 2MnO_2 + 2O_2$$

This explanation, however, does not hold good in many cases. In the inversion of sugar, for example, it can hardly be

* Phil. Trans. 151, 855.
** Memoirs and proceedings of the Chem. Soc. 1848.
† Reprints of the British Assn. 10 Part I, 32.

believed that the dilute acid forms an intermediate compound. Nor is it possible to understand how enzymes in such infinitismal quantities can form an intermediate compound. It is more plausible to assume that when sugar breaks down to dextrose and laevulose, it does so through the influence of the hydrogen ion of the dilute acid, as suggested by that eminent chemist Svante Arrhenius.‡ Paul Sebatier and others have also studied the catalytic influence of ionic hydrogen on various organic compounds, proving beyond doubt that the hydrogen ion acts as a catalyst. More recently, however, this phenomenon has been studied by Biddle* in connection with the change of cinchonine and quinine to cinchotoxine and quinotoxine, respectively, by the catalytic action of weak acids. This is one of the most remarkable examples of catalysis of ionic hydrogen. Nor can we explain the remarkable catalytic action of some of the radio-active substances by assuming the formation of an intermediate compound. The catalytic power of light in photography can neither be explained by its temporary combination with any of the reacting components. In all such cases the changes may be attributed to electric energy rather than simply to the formation of an intermediate compound.

Actino-catalysis provides some of the most interesting phenomena we meet with in our every-day life. The beautiful coloring of leaves, flowers and fruits is partly due to the catalytic action of sunlight. When plants are grown in the dark the difference in color is markedly noticeable. The color of the skin of various peoples of the world is also a phenomenon of actino-catalysis. The pigment of the skin is more or less determined by the light of the sun. The physiological effect of light on the eyes is probably due to actino-catalysis. The progressive chlorination of methane, CH_4, is one of the well known examples of actino-catalysis. This is so characteristic of the aliphatic series that in the case of homologues of benzene, the chlorination takes place in the aliphatic side-chain in the presence of light. In the absence of light, on the contrary, chlorine enters the benzene ring, as shown by Slater.**

‡ Z. Phys. Chem. 4, 226.
* Jour. Am. Chem. Soc. 34, 500, and Science 32, 486, 1910.
** Z. Phys. Chem. 45, 513.

The term catalysis is really confusing. It means breaking down. Catalysis is neither the breaking down of a substance nor building it up. We use the term as applied to every form of a reaction, be it synthetic, analytical or reversible. Some times the change takes place in the body of the catalyst itself, and sometimes in the reacting components. It should rather be called a chemical induction, as the mere presence of a substance induces the chemical reaction. Ostwald* compares it with the "whip on a horse," or with "oil on the wheels" of a rusty machine, thus comparing it with induction.

Catalytic reactions may be classified in three main groups as follows: (a) addition reactions; (b) reactions of polymerization; (c) reactions of substitution. The following examples may be given as representing the above three groups:

(a) $C_6H_6+CCl_3CHO+Al_2C1_6=C_6H_5CCl_2CHO.\ HCl+Al_2Cl_6$**

(b) Polymerization of China wood oil by its own oxidation-products,† or the polymerization of Pinene by sunlight. When iodides of pinene are allowed to stand in the sunlight, iodine is liberated and pinene polymers are formed.‡

(c) The obtaining of diphenylmethane and anthracene from benzene and formaldehyde by dehydration is a case of substitution as will be seen by the following equation:

$$4C_6H_6+3CH_2O=CH_2(C_6H_5)_2+C_{14}H_{10}+3H_2O+H_2$$

The following are the general characteristics of catalysis as compiled by Mellor in his book on chemical statics and dynamics:

1. The catalyst has the same chemical composition at the beginning as at the end of the reaction. The physical state of the catalyst may, however, change. This is found when crystalline MnO_2 is heated with $KClO_3$ and is reduced to powder form.

2. A small quantity of a catalytic agent is sufficient to effect the transformation of an indefinitely large quantity of the reacting substance. Ernst¶ has shown that a solution of .0004 g

*Ueber Katalyse.
**Combes Bull. Soc. 45, 226, or Frankforter & Kritchevsky Jour. Am. Chem. Soc. 36, 1517.
†Schuman Jour. Ind. & Eng. Chem. Jan. 1916.
‡Frankforter & Poppe Com. Eighth Int'l. Cong. of Appld. Chem. XXV, 363.
¶Zeit. Phys. Chem. 37, 448.

of colloidal platinum will bring about the combination of ten litres of a mixture of hydrogen and oxygen. According to Kastle and Beatty* .000001 g of $KMnO_4$ in 10c.c. solution accelerates the reduction of Mercuric chloride by oxalic acid.

3. A catalytic agent is incapable of starting a reaction; it can only modify the velocity of the reaction.

4. A catalytic agent cannot effect the final state of equilibrium of opposing reactions.

5. The velocity of two inverse reactions is affected by the catalyst to the same extent.

6. The state of equilibrium is independent of the nature and quality of the catalytic agent.

These are general characteristics and none of them are definite. Objections can be brought against every one of the above characteristics.

Thus far only the positive side of catalysis has been considered. There is, however, another or negative side, in which the reaction is retarded, instead of being accelerated. For instance, Bunsen and Roscoe** have shown that if the reacting gases, like chlorine and hydrogen are mixed with a foreign gas, like oxygen, the rate of transformation of hydrogen and chlorine is retarded to a remarkable degree. If we consider both the positive and negative aspects of catalysis, we can say with Ostwald,† that "There probably is no kind of chemical reaction which cannot be influenced catalytically, and there is no substance, element or compound, which cannot act as a catalyser."

Friedel and Crafts' Reactions

Although Mercer was the first to use metals in catalytic reactions, it was Playfair, who first used aluminium in a catalytic experiment, a fact which finally culminated in the discovery of Friedel and Crafts' reaction, and in the "New Phase," upon which the work of this thesis is based. Playfair's experiment in his own words runs as follows:

"If a piece of calico dyed with indigo is dipped in nitric acid, no change occurs; but if placed in nitric acid containing

*Am. Chem. Jour. **24**, 182.
Pogg. Ann. **96, 373, and Phil. Trans. **146**, 355.
†Zeit. Electric Chem. **7**, 995, and Nature **65**, 522.

an aluminum compound, presumably alumina, the blue color is immediately discharged."

Upon this simple discovery was based the reaction of Friedel and Crafts which later found such a wide application in organic synthesis. Friedel and Crafts* found that when small quantities of anhydrous aluminum chloride were added to amylchloride, a violent reaction took place and hydrochloric-acid was evolved in abundance, the reaction resulting in the formation of a saturated hydrocarbon of the general formula C_nH_{2n+2}. Bu when the reaction was conducted in the presence of a hydrocarbon, the resulting compound was found to be a combination of two radicals, one of the hydrocarbon, and the other of the chloride. Thus benzene and amylchloride in presence of aluminum chloride gave amylbenzene.

$$C_5H_{11}Cl + C_6H_6 + Al_2Cl_6 = C_5H_{11} - C_6H_5 + HCl + Al_2Cl_6.$$

Since the discovery of this reaction chemists have used it in various ways, particularly in connection with the condensation of aromatic hydrocarbons with other organic compounds, such as alkyl halides or acid chlorides. In all such cases, however, a halogen compound is used, together with a hydrocarbon and hydrochloric acid is evolved in the reaction. Thus a hydrocarbon, an aldehyde, a ketone and an acid may be formed according to the following equations:

$$C_6H_6 + CH_3Cl + Al_2Cl_6 = C_6H_5 - CH_3 + HCl + Al_2Cl_6.$$

$$C_6H_5CH_3 + CO + HCl + Al_2Cl_6 = C_6H_4 - CH_3CHO + HCl + Al_2Cl_6.$$

$$C_6H_6 + CH_3COCl + Al_2Cl_6 = C_6H_5COCH_3 + HCl + Al_2Cl_6.$$

$$C_6H_6 + COCl + Al_2Cl_6 = C_6H_5\ COC\ l \longrightarrow C_6H_5COOH + HCl + Al_2Cl$$

The synthesis of Anthraquinone from pthalic-anhydride and benzene is very interesting, as it is apparently a dehydrating reaction. But it must be noted that both aluminum chloride and sulphuric acid are used to bring about the reaction. Under these conditions, can it reasonably be said, that the dehydrating action is due to aluminum chloride alone? Why could it not be due to sulphuric acid, a well known dehydrating agent? Besides, there are two distinct steps in the reaction as shown below

* Comp. rend. 84, 1399, 1877.

and how can either of the steps be attributed to the action of only one of the reagents used, be it sulphuric acid or aluminum chloride? It is difficult to understand how aluminum chloride alone is responsible for the second step.

$$C_6H_4\begin{matrix}/CO\\\backslash CO\end{matrix}>O+C_6H_6=C_6H_4\begin{matrix}<CO-C_6H_5\\\backslash COOH\end{matrix}$$

$$C_6H_4\begin{matrix}<CO-C_6H_5\\\backslash COOH\end{matrix}-H_2O=C_6H_4\begin{matrix}<CO\\\backslash CO\end{matrix}>C_6H_4 \quad (II)$$

It is interesting to note that in Friedel and Crafts' reaction, a larger quantity of aluminum chloride is required, than would be justified as a catalyst. This has thrown some doubt upon the fact of aluminum chloride being the catalyst. But recently Steele* has pointed out that though a large amount of aluminum chloride is required, that fact does not necessarily preclude the action of it as a catalyst, if it can be shown that it forms a stable compound with the product. He has also accounted for the disappearance of aluminum chloride in the reaction by attributing it to independent side reactions.**

Friedel and Crafts did not explain their reaction satisfactorily and even today the problem has not been satisfactorily solved. Gustavson,† however, showed that intermediate organo-aluminum compounds were formed, which later broke down, liberating the condensed hydrocarbon, and regenerating aluminum chloride.

$$C_6H_6+Al_2Cl_6=C_6H_5Al_2Cl_5+HCl$$
$$C_6H_5Al_2Cl_5+C_5H_{11}Cl=C_6H_5C_5H_{11}+Al_2Cl_6.$$

However there was not sufficient data in his hands to prove absolutely the formation of intermediate compounds.

Aluminum chloride alone is used for a variety of purposes, besides being used in the Friedel and Crafts' reaction proper. For instance, it has been used for effecting an internal condensation by Kipping,‡ thus:

$$C_6H_5CH_2.CH_2.CH_2.CH_2.COCl+Al_2Cl_6=$$
$$C_6H_4\begin{matrix}<CH_2-CH_2\\\backslash CO-CH_2\end{matrix}>CH_2+HCl+Al_2Cl_6.$$

* Trans. Chem. Soc. **83**, 1471-90.
** Ibid.
† Bull Soc. Chem. **42**, 325, or Ber. **13**, 157.
‡ Trans. Chem. Soc. **65**, 484, and **75**, 144.

Scholl and Seer ¶ have shown that anhydrous aluminum chloride actually breaks off free hydrogen, instead of hydrochloric acid, in some cases.

$$C_5H_{12}+Al_2Cl_6=C_5H_{10}+H_2+Al_2Cl_6.$$

Page† has shown that aluminum chloride possesses the power of transporting the chlorine atom to certain organic compounds. This has been found in case of pyridene and trioxymethylene, as will be shown later. Jacobsen* has shown that aluminum chloride reverses the condensation-reaction under suitable conditions. Thus in the case of hexamethylbenzene, for instance, the methyl groups are successively detached, forming all the lower homologues of benzene.

Another very interesting phenomenon has been observed by Anchütz,** in connection with the use of aluminum chloride. He has observed that aluminum chloride, not only detaches the methyl groups from the higher homologues of benzene, thus reducing them to lower homologues and finally to benzene itself, but it also builds up other homologues, both isomeric and higher in transplanting the methyl groups from one position to another. Thus m-xylene gives toluene, p- and o-xylenes and pseudocumene.

The new phase of catalysis:

It was discovered by Frankforter and Poppe‡ that anhydrous aluminum chloride had dehydrating properties like that of sulphuric acid and that it could be used instead of sulphuric acid in condensation reactions. When pinene, chloral and aluminum chloride were brought together at the ordinary room temperature, there was a vigorous reaction, giving ultimately substances, which did not contain oxygen. As such a reaction could be explained only by the elimination of water, it was supposed that aluminum chloride must have served, at least, partially as a dehydrating agent. On this assumption various experiments were conducted by them in the study of this new phase of aluminum chloride. This work was later taken up by Frankforter and Kritchevsky.

¶ Monatch 33, 1.
† Ann. Chem. Phys. 225, 196.
* Ber. 18, 339.
** Ann. 235, 177-192.
‡ Orig. Comm. of the Eighth Intn'l Cong. of App. Chem. 1912.

Frankforter and Kritchevsky first thought of studying some of the reactions that had already been studied in connection with dehydration. Baeyer had studied extensively the dehydrating action of sulphuric acid in condensation reactions. One of the most natural experiments that suggested itself to them, was, that between chloral and aromatic hydrocarbons, as Baeyer¶ had worked with them in that line. For instance, Baeyer, working with benzene and chloral, obtained diphenyltrichlorethane. On looking over the literature, however, they found that the reaction of aluminum chloride on benzene and chloral had been studied by various investigators, such as, Combes, Biltz. Boeseken and Dinesmann. These investigators had obtained entirely different results from each other. Thus, Combes* obtained no less than four different substances, namely:

$(C_6H_5)_2CH-CCl_3.HCl$, $(C_6H_5)_2CH-CHCl_2$, a compound of the formula $C_{22}H_{17}Cl$, $(C_6H_5)_4C_2H_2$. But Biltz** obtained three substances, namely: $C_2H_2(C_6H_5)_4$, $(C_6H_5)_2C=CCl_2$, and triphenylvinylalcohol $(C_6H_5)_2C=C(OH)C_6H_5$. While Dinesmann† obtained a reaction, which he expressed as follows:
$C_6H_6+OCH-CCl_3=C_6H_5(OH)CH-CCl_3$ a compound obtained by Jotsitch‡ from Grignard reaction.

Strange as it may appear, none of these investigators, although studying the same reaction as that of Baeyer, seemed to have discovered the dehydrating action of aluminum chloride. At least, none of them ever said a word about dehydration in their respective papers. After studying the reaction very carefully, in every case Frankforter and Kritchevsky§ showed that their assumption was verified, and that the reaction with aluminum chloride was found to be much more simple than was previously considered. They also showed that aluminum chloride, not only acted as a simple dehydrating agent, but also as a catalyst in some of the reactions. For example, in one case, not only diphenyltrichloroethane, but also a substance of the formula $C_6H_5CCl_2$-CHO.HCl identical with that obtained by

¶ Ber. 5, 1098.
* Bull 45, 226.
** Ber. 26, 1952.
† Compt. Rend. 141, 201.
‡ J. Russ. Phys. Chem. Soc. 34, 96.
§Jour. Am. Chem. Soc. 36, 1516.

Combes, was obtained. This could be explained only by catalysis and not by dehydration. It was further found to be as universal as sulphuric acid in its application as a dehydrating agent.

Notwithstanding the fact that aluminum chloride has been used by many in reactions with oxy-compounds, aldehydes and ketones, except chloral, have hardly been used in this connection. Walker and Spencer§ have shown that aluminum chloride dissolves in organic compounds, especially those containing more than one oxygen atom, giving additive compounds with aluminum chloride. Thus they obtained organo-aluminum compounds of ethers, acetic acid, anisol, phenetole, etc.

It must be pointed out, however, that Eugene Wass† stated in his work with dichlorether and benzene, whereby he obtained hydrocarbons of the formulae $C_{20}H_{18}$ and $C_{14}H_{14}$, that aluminum chloride acted as a dehydrating agent. It is interesting to see that he expressly uses the word "liess mich vermuten." By treating dichlorether alone, he says, he obtained an oil resembling in properties monochloraldehyde. Evidently either the reaction was very complex or the dichlorether was not pure enough. In any case, it cannot be explained how he obtained monochloraldehyde by the action of aluminum chloride on dichlorether, because the action of aluminum chloride in that reaction is neither dehydrating nor catalytic. Even supposing that dehydration took place in the second step of the reaction, that is, between monochlor-aldehyde and benzene, it is difficult to understand how he obtained hydrocarbons, instead of chlor-compounds. With benzene and chloral diphenyltrichlorethane was obtained in this laboratory and not a hydro-carbon.

It will thus be seen that the dehydrating properties of aluminum chloride were not known to previous investigators, and if known at all, as in the case of Wass, it was only a vague assumption, which the authors never tried to verify by further experiments. Frankforter and Kritchevsky were thus justified in calling their reaction as "New Phase" of catalysis. The new

§ Trans. Chem. Soc. 85, 1082.
†Ber. 15 (1), 1128.

reaction is identical in effect with Baeyer's reaction. The relationship between Friedel and Crafts' reaction and Grignard's reaction on the one hand, and Baeyer's reaction and the "New Phase" of catalysis of Frankforter and Kritchevsky on the other, can thus be tabulated:

Friedel and Crafts

$$C_6H_6+OCH\text{--}CCl_3+Al_2Cl_6=C_6H_5-CH(OH)CCl_3+Al_2Cl_6$$

Grignard

$$C_6H_6+Mg+I_2+OCH-CCl_3=C_6H_5-CH\ (OH)CCl_3+MgI_2$$

Baeyer

$$2\ C_6H_6+OCH-CCl_3+H_2SO_4=(C_6H_5)_2CH-CCl_3+H_2O+H_2SO_4$$

Frankforter & Kritchevsky

$$2\ C_6H_6+OCH-CCl_3+Al_2Cl_6=(C_6H_5)_2CH-CCl_3+H_2O+Al_2Cl_6$$

Extension of "New Phase":

The following research was taken up to study this "New Phase" of catalysis, that is, the dehydrating action of aluminum chloride in the reaction of aldehydes with other organic compounds. Halogen compounds, whether alkylhalides, acid chlorides or chlorine substituted ethers or aldehydes, were invariably used in Friedel and Crafts' reaction. It was thought, therefore, of studying this "New Phase" on simple aldehydes without any chlorine in them. Thus the reaction of formaldehyde on organic compounds first suggested itself. As formaldehyde was very inconvenient to work with, it was decided to use trioxymethylene instead. The study of formaldehyde, however, was taken up later, in order to determine whether or not its reaction was identical with that of trioxymethylene.

On going over the literature of both formaldehyde and trioxymethylene, it was found that none of them had been used with aluminum chloride, although chloral and dichlortrioxymethylene were. Formaldehyde, as such was studied by Baeyer in his reaction, and by several others who repeated his work. It was also studied in connection with its reaction on cyclohexanol in presence of hydrochloric acid by Marcel Murat and Cathala,* in which they obtained a compound of the formula

* J. Pharm. Chem. VII, 6, 289-292.

$C_6H_{11}O\text{-}CH_2\text{-}OC_6H_{11}$. It was studied by Madsen** in preparing methylenedisalicylic acid from formalin and salicylic acid in the presence of hydrochloric acid. But the behavior of formaldehyde had never been studied in the presence of aluminum chloride. Much less had been done with trioxymethylene. It had neither been used by Baeyer in his reaction, nor by any others, even in the presence of hydrochloric acid. Much less, therefore, had it been used in the presence of aluminum chloride. It was, however, found that Grassi and Maselli† had used dichlortrioxymethylene with benzene in the presence of aluminum chloride, and had obtained diphenylmethane. They had obtained trioxymethylene hydrate $CH_2(OCH_2OH)_2$ by treating trioxymethylene with water and acetic acid. By further treating this hydrate with hydrochloric acid, they obtained dichlortrioxy methylene. They assumed that hydrochloric acid broke down the ring compound into formaldehyde, at the same time forming a hydrochloric $ClCH_2OH$. This latter compound they believed then reacted with benzene, forming dyphenylmethane. They failed to prepare any of the oxycompounds.

The molecular structure of trioxymethylene is generally considered to be a ring compound, in which the oxygen and the methylene groups are symmetrically arranged. In case the accepted theory is a fact, it was hoped to prepare condensation products by breaking the ring and substituting hydrocarbon radicals for one or more of the oxygen atoms, as indicated by the following formulae:

$$CH_2\begin{matrix}<0.CH_2.R\\<0.CH_2.R\end{matrix} \qquad 0\begin{matrix}<CH_2.R\\<CH_2.R\end{matrix} \qquad \text{and } CH_2\begin{matrix}<R\\<R\end{matrix}$$

It is well known that trioxymethylene acts quite differently from other aldehydes. It absorbs dry hydrochloric acid, giving dichlormethylether, $(CH_2Cl)_2O$. Treated with hydrochloric acid at one hundred degrees, it breaks down into CH_3Cl and H.COOH. It also gives dithiotrioxymethylene $(C_3H_6S_2O)_2.H_2O$, by treatment with H_2S.

Littlerschied and Thimme* have shown the difference of behavior of trioxymethylene with hydrochloric acid, as com-

** Arch. Pharm. **245**, 42-48.
† Gaz. **28**, 477, 1898.
*Ann. 334, 1-49.

pared with that of formaldehyde, methylal, etc. Auerbach and Barschall** have also shown the difference of behavior of trioxymethylene from formaldedyde and other polyoxymethylenes.

Such considerations as these strengthened the hope of obtaining some oxycompounds from the reaction. But in none of the experiments oxycompounds could be prepared. The reaction of trioxymethylene and the hydrocarbons varies widely, depending upon the conditions under which the reaction takes place. This might perhaps account for not obtaining oxycompounds.

It might be of interest to note here that trioxymethylene, though never studied in connection with Friedel and Crafts' reaction, has been studied in connection with the Grignard's reaction, which is so similar to Friedel and Crafts', as shown in the preceding table. Grignard, together with Tissier* obtained primary alcohols from the reaction of trioxymethylene and organo-magnesium compounds in ether solution. Thus they obtained propyl alcohol from trioxymethylene and magnesium ethyl bromide, butyl alcohol from trioxymethylene and magnesium propyl bromide, benzyl alcohol from trioxymethylene and magnesium benzyl bromide, etc.

Tiffenean and Delange† repeated the experiments of Grignard and showed that the benzylalcohol obtained by Grignard was not the normal product, but was isomeric with o-tolylcarbinol. They further showed that this abnormal behavior was peculiar to trioxymethylene, all other aldehydes giving the normal product.

Paul Carre‡ obtained mesitylcarbinol $C_6H_3(CH_3)_2.CH_2OH$, dixylylethane, mesitylene and dixylymethylether by reacting trioxymethylene with magnesium mesitylbromide.

Thus trioxymethylene has never been used before, either with sulphuric acid or with aluminum chloride and consequently no condensation products have ever been made. It will be shown in this paper that no oxycompounds could be prepared from

** Chem. Cent'l. 1907 II, 1734-1735.
* Compt. Rend. 134, 107-108.
† Compt. Rend. 137, 573-575.
‡Compt. Rend. 151, 149.

trioxymethylene and other organic compounds, though such a thing was expected. It will further be shown that trioxymethylene reacting on organic compounds in the presence of aluminum chloride in many instances gives the same condensation products as formaldehyde gives in the presence of sulphuric acid. It will also be shown that formaldehyde reacts similarly on organic compounds, whether in the presence of sulphuric acid or aluminum chloride.

EXPERIMENTAL.

General Method:

The method used in preparing the compounds was as follows: The two reacting substances were mixed together in a definite proportion in a flask, and then powdered andydrous aluminum chloride was added piece-meal to the required extent at ordinary temperature, except in a few cases where the temperature was kept near zero. Hydrochloric acid gas was liberated in great quantities in every case. The mixture was stirred constantly, either by hand or by some automatic device. The reaction was allowed to take place for an hour or two, until all the aluminum chloride was added, and then the flask was kept at room-temperature for three or four days, to allow the completion of the reaction. Afterwards the product was treated with ice-cold water and sometimes with pieces of ice if the temperature seemed to rise fast enough. The oily layer that arose to the surface of the water was separated from it, washed several times with water to remove all hydrochloric acid, dried, and then subjected to distillation. It was sometimes distilled with steam, sometimes in *vacuo*, as the particular case demanded. In some cases alcohol, ether or acetone was added to the oily layer, to see if anything could be precipitated out, and if so, it was precipitated, and purified by redissolving and reprecipitating several times, and finally when found pure enough, was analyzed. If much material remained in the filtrate, it was subjected to distillation. Nothing was looked for in the water, except when it was suspected that it had dissolved some of the product.

The reaction of trioxymethylene on hydrocarbons was as a rule very simple, and the same condensation products were

obtained as had been by Baeyer with formaldehyde, and by Friedel and Crafts with methylene chloride.

$$4R.H+(CH_2O)_3+Al_2Cl_6=CH_2(R)_2+$$
$$R(CH)_2R+3H_2O+H_2+Al_2Cl_6$$

Benzene and Trioxymethylene:

To 500 cc of benzene in a beaker were added 35 grams of trioxymethylene, and the mixture cooled to zero by surrounding with ice and water. An automatic device kept the mixture stirred continuously and three or four grams of aluminum chloride were added every few minutes, until about 170 grams were added. The stirring was continued for about seven hours—the temperature never rising above 20 degrees, and most of the time it was below 10 degrees.

After about 50 grams of aluminum chloride had been added, the color of the mixture changed to a reddish brown and copious fumes of hydrochloric acid gas were liberated. After the stirring was stopped, hydrochloric acid still continued to pass off. The mixture was then kept in a refrigerator for three or four days. At the end of that time, it was removed and ice water was added in order to decompose the product and dissolve the aluminum chloride. After a sufficient quantity of water was added, an oily substance, with an aromatic smell, separated out and floated on the surface of the water, while some solid substance remained at the bottom of the flask. There was also some solid material, lighter than water, but heavier than oil, which distributed itself between the two layers. The whole mass was then extracted with ether. All dissolved, except the solid substance at the bottom of the flask, and two layers, one of the water and one of the ether extract, were visible. The ether solution was then separated from the water and the insoluble substance, which was set aside for further treatment.

The ether extract, after being dried, was subjected to fractional distillation at ordinary pressure and the distillates were collected as follows: (a) between 40°-80°, (b) 80°-130°, (c) 250°-280°, and (d) 280°-360°. A preliminary examination showed that distillate (a) was largely ether with benzene. Distillate (b) was largely benzene with dissolved hydrochloric acid. After distilling

the fraction (b) the temperature suddenly rose from 130° to 250°, and an aromatic liquid continued to distill over, until the temperature of 280° was reached. Then a yellowish white substance of a somewhat waxy nature passed over and solidified on the cool walls of the condenser. This substance continued to distill until the temperature had reached 360°. Distillation was then stopped, as the tarry resinous material remaining in the flask showed signs of decomposition. A peculiar blue fluorescence was observed in the distillate. The tarry material was set apart for further treatment.

As the yield of products was not quite satisfactory, the above experiment was repeated, varying the conditions of temperature and the proportion of trioxymethylene to benzene. In all the cases the same products were obtained, although the yield of the liquid and solid distillates (c) and (d) varied in each case. In the above experiment, for instance, the liquid distillate (c) was rather small as compared with those in other cases. When 40 grams of trioxymethylene were used under exactly similar conditions, the yield of both (c) and (d) distillates was greater, and when 50 grams of trioxymethylene were used, there was a still greater yield. On the contrary, when 100 grams of trioxymethylene were used, there was a very good yield of the liquid distillate (c), but not enough of the solid distillate (d). Even when the temperature of the reaction was as high as 50 degrees, the same products were obtained, although the yield of the two distillates varied.

The liquid distillate (c) was redistilled, after which it showed signs of crystallization. The redistilled aromatic oil was cooled in a freezing mixture, when it crystallized in colorless prismatic needles, with the melting point between 26° and 27° degrees. It was at once suspected to be diphenylmethane. Hence it was compared with Kahlbaum's diphenylmethane in appearance, crystalline form, boiling point and other characteristics. Kahlbaum's diphenylmethane, although marked "C.P.", was found to be impure. It was a yellowish colored liquid, which began to distill at 254°, and continued to distill until 261°. After distillation, however, it became colorless and crystallized at once, in colorless, prismatic needles, with m.p. 26°-27°.

The diphenylmethane prepared in this laboratory, distilled

between 259° and 262°. It was perfectly colorless and crystallized at once. The various tests indicated that it was diphenylmethane. It is interesting to note that all the homologues of diphenylmethane have a tendency to oxidation in the air, probably in the presence of light; for diphenylmethane and its homologues become yellowish in color after being kept for some time.

Baeyer* was probably the first to obtain diphenylmethane by the action of formaldehyde on benzene in the presence of acetic and sulphuric acids. Later Friedel and Crafts** obtained the same thing by the action of methylene chloride CH_2Cl_2 on benzene in the presence of aluminum chloride. Grassi and Maselli† obtained it by the action of dichlortrioxymethylene on benzene in the presence of aluminum chloride. Very recently Nastukoff‡ repeated Baeyer's experiment and showed that phenylformol was formed as a result of the reaction between formaldehyde and benzene, which on dry distillation yielded, not only diphenylmethane, but also toluene, xylene, anthracene and synanthrene.

The solid distillate (d), which passed over between 280° and 360°, was finally dissolved in a mixture of hot benzene containing a little alcohol, as this mixture was found to give the best results. On cooling the solution, a leafy white substance with pearly lustre crystallized out. This was filtered out, washed with alcohol several times to remove the last traces of diphenylmethane, and lastly recrystallized three or four times. The pure crystals thus obtained melted at 210°-211°. The crystals in and out of the solution, showed a beautiful blue fluorescence, and were monoclinic in structure. The analysis of the substance gave:

Found C = 94.50; H = 5.65. Cal. for $C_{14}H_{10}$. C = 94.38;
H = 5.62

Kahlbaum's Anthracene as compared with that prepared in this laboratory melted at 212°-213°. Both give identical anthraquinones and anthracene picrates in red needles, which decomposed by the addition of more alcohol. All other tests, both physical and chemical, confirmed it to be anthracene.

* Ber. 5, 1099, 1872, and Ibid 6, 220-224.
** Ann. Chim. Phys. VI, 2, 263-277, 1887.
† Gaz. 28, 477-500, 1899.
‡ J. Russ. Phys. Chem. Soc. 35, 825, 1903.

Baeyer obtained hydro-anthracene, which probably changed to anthracene on distillation. Nastukoff, who repeated his experiments, also obtained anthracene. Friedel and Crafts obtained it by action of methylene chloride on benzene. Anschütz* on the other hand, obtained it by the action of acetylenetetrabromide on benzene in the presence of aluminum chloride. But more interesting is the fact that Dewar and Jones** obtained anthracene by the action of nickel carbonyl on benzene in the presence of aluminum chloride. Of course, they did not get diphenylmethane, but instead, obtained benzaldehyde.

The fact that diphenylmethane and anthracene are the two principal compounds formed in the reaction, throws some light on the nature of the reaction, although the third compound yet to be isolated from the resinous tar, is not considered. If justifiable from the data at hand, the reaction can be explained thus:

$$4C_6H_6+(CH_2O)_3+Al_2Cl_6=CH_2(C_6H_5)_2+$$
$$C_{14}H_{10}+3H_2O+H_2+Al_2Cl_6.$$

As both diphenylmethane and anthracene were formed in this reaction, it was concluded that either the trioxymethylene molecule must not be symmetrical, or else, diphenylmethane must give anthracene by a further action of trioxymethylene on it. Baeyer had obtained dihydro-anthracene by treating diphenylmethane with formaldehyde in the presence of sulphuric acid. In order to determine whether or not trioxymethylene, gives anthracene by reacting on diphenylmethane, the following experiment was tried:

Diphenylmethane and trioxymethylene:

To 50 grams of diphenylmethane, 9 grams of trioxymethylene were added and then 20 grams of aluminum chloride, added piecemeal. Hydrochloric acid gas was liberated in abundance, showing that the reaction was taking place. After the reaction was complete, the product was treated with water, as mentioned before. The oily layer extracted with ether, separated from the water, and the ether extract subjected to distillation. Nothing was obtained from the distillates, except ether and unchanged diphenylmethane. The distilling was discontinued when the tem-

* Ann. 235, 176.
** Trans. Chem. Soc. 85, 213-222.

perature reached 400°. The residue that remained in the distilling flask was a resinous, tarry substance, identical with that obtained from benzene and trioxymethylene. This may perhaps mean that the tarry matter is a condensation product of diphenylmethane and trioxymethylene. This experiment proves that anthracene is not formed by the further action of trioxymethylene on diphenylmethane, as was the case in Baeyer's experiment, when anthracene was formed by the action of formaldehyde on diphenylmethane. This experiment shows that, either the trioxymethylene molecule is unsymmetrical, or that it acts abnormal in certain cases. Whichever it may be, the fact is, that trioxymethylene does not act on diphenylmethane in the presence of aluminium chloride, like formaldehyde in the presence of sulphuric acid.

Benzene and Trioxymethylene:

The tarry residue that was set apart for further treatment, was now taken up for examination. It was dissolved in chloroform, in which it was almost completely soluble, and the insoluble material, if any, was separated by filtration. The clear, dark filtrate, when acetone or methyl alcohol was added, the color changed to a dark brown, resulting in a colloidal solution. When a drop of hydrochloric acid was added and the solution shaken, a dark brown precipitate separated. This reprecipitated several times, vaporized at above 130°, but did not show a definite melting point. It was found to be extremely difficult to obtain a large quantity of this material, as it precipitated a sticky mass. Hence, the bromine derivative was prepared by the action of bromine, which reacted with it vigorously. The product was treated with water to remove any excess of bromine and the residue, after being dried, was dissolved in chloroform. Only resinous material was obtained after evaporation. The addition of alcohol or acetone to it precipitated a yellowish brown powder. After several reprecipitations, the substance was found to be still impure, shrinking at about 160°, but decomposing at between 180°-200°. So the brown powder was washed with ether several times, until the filtrate showed no precipitation upon the addition of alcohol. The precipitate from this ether filtrate was yellow and vaporized at 140°-150°. The residue left on the filter paper, after

washing with ether, shrank at 150°, and decomposed at 200°. An analysis of the compound and its bromine determination gave $C_{4\cdot2}H_2Br$, as the empirical formula. This formula does not agree with any of the theoretical possibilities. This may mean that the compound was not pure enough to give any definite data.

In order to study whether or not trioxymethylene forms similar compounds with other hydrocarbons in the presence of aluminum chloride, the following experiments were conducted, substituting other organic compounds instead of benzene:

Toluene and Trioxymethylene:

Fifty grams of trioxymethylene were suspended in 400 c.c. of toluene in a beaker and 100 grams of aluminium chloride were added piecemeal, at an ordinary temperature. A large amount of heat was liberated, but the temperature was not allowed to rise above 65 degrees. The whole mass changed to a reddish brown color, and abundant fumes of hydrochloric acid were given off. The upper layer showed a deep blue fluorescence. The product was kept in a cool place for four days and after treating with ice water, was subjected to the same process described under benzene. Then it was distilled under ordinary pressure and the distillates were collected thus. (a) between 50°-120°, (b) between 290°-310°, and (c) between 310°-400°. The distillate (a) was found to consist of ether, toluene, benzene and a few drops of xylene. After the distillate (a) passed over, the temperature at once arose to 290°. At this point an oil began to distill over, until a temperature of 310° was reached. Then a semi-solid, yellowish and waxy in nature, began to distill and solidify on the walls of the condenser. The solid continued to pass over, until a temperature of 400° was reached. Owing to signs of decomposition, the distilling was discontinued. A dark resinous substance remained in the flask as in the case of benzene. This was set aside for further investigation.

The oil collected between 290° and 310° on redistillation passed over at 285° and 287°. It was a colorless, odorless oil, with a brilliant blue fluorescence. It could not be crystallized, even after cooling to zero. On analysis it gave numbers for $C_{15}H_{16}$ or ditoluylmethane. Both physical and chemical prop-

erties corresponded with those of ditoluylmethane, a substance obtained by Friedel and Crafts from methylenechloride, toluene and aluminum chloride. Weiler* obtained the same thing by Baeyer's reaction from methylal and toluene.

The semi-solid distillate (c) was dissolved in a mixture of alcohol and benzene and crystallized from it. The crystals were yellow scales, monoclinic in structure. This substance was recrystallized several times, until there was no change in the melting point. The crystals, thus purified, melted at 225°-226°. Analysis and general properties checked well for dimethylanthracene, a compound prepared by Friedel and Crafts, by treating toluene and methylenedichloride with aluminum chloride. It is interesting to note that Anschütz obtained the same substance by treating toluene and acetylenetetrabromide with aluminum chloride. The dimethylanthracene obtained by Friedel and Crafts and Anschütz was of a yellow color with a melting point at 225°-226°. Friedel and Crafts obtained the same substance by treating toluene and benzalchloride and aluminum chloride Wachendorff and Zincke* obtained the same dimethylanthracene. Levaux‡ repeated almost all the experiments of previous investigators in connection with ditoluylmethane and dimethylanthracene. He obtained the same dimethylanthracene by different methods. He also showed that ditoluylmethane, by further action of methylenedichloride and aluminum chloride, changed to dimethylanthracene, and that anthracene formed a compound with aluminum chloride of the type of

$$C_6H_4 \begin{matrix} \diagup CH.AlCl_2 \\ \diagdown CHCl \end{matrix} \diagup C_6H_4$$

It is much more interesting to note that Anschütz and Immenddorf† obtained the same dimethylanthracene by toluence and aluminum chloride alone.

As this reaction is evidently an exact duplicate of the reaction with benzene, it may be represented as follows:

$$4C_6H_5.CH_3+(CH_2O)_3+Al_2Cl_6=$$
$$CH_2(C_6H_4.CH_3)_2+C_{16}H_{16}+3H_2O+H_2+Al_2Cl_6.$$

* Ber. 7, 1181-1189.
**Ber. 10, 1482.
‡Ann. Chim. Phys. (VIII) 20, 433-508.
† Ber. 17, 2816.

o-Xylene and Trioxymethylene:

To a mixture of 500 grams of o-xylene B.p. 142 and 50 grams of trioxymethylene, 100 grams of aluminum chloride were added piecemeal at ordinary temperature and with constant stirring. During the reaction, the temperature arose to 65° and copious fumes of hydrochloric acid were liberated. The upper layer of the product showed a deep greenish-blue fluorescence, while the lower was dark brown in color. After the product was allowed to stand at ordinary room temperature for three days, the reaction seemed to have been complete. It was then treated with icewater and extracted with ether. After separating the ether extract from the water, it was distilled at ordinary pressure. The distillates were collected as follows: (a) between 70°-150°, (b) 200°-330°, (c) 330°-400°. After these distillates were removed, there remained in the flask a tarry substance, as in previous instances. Distillate (a) consisted of a mixture of hydrocarbons, like benzene, toluene, xylene and pseudocumene The distillate (b) when redistilled gave fractions: (1) 308°-310°, (2) 311°-313°, (3) 314°-316°, (4) 325°-350°. All these fractions showed a wonderful blue fluorescence, much more so than in the case of diphenylmethane and ditoluylmethane. The fraction that passed over between 311°-313° was redistilled several times and then analyzed. Analysis gave numbers for $C_{17}H_{20}$, or dixylylmethane, a compound prepared for the first time in this laboratory. This compound, nor any of its isomers, have ever been made before, although a substance of the same empirical formula, a durylbenzyl compound has been prepared by Friedel and Crafts and Ador*. It is rather strange that Friedel and Crafts should not have obtained this compound by the reaction of methylenedichloride on xylene in the presence of aluminum chloride. The molecular weight of dixylylmethane was not determined by the usual methods. However, it was calculated from Longenescu's formula:

$$\frac{T}{100D} = n \text{ and } \frac{T}{M} = 37, \text{ for liquids, where } T =$$

the absolute melting point or boiling point, D=density, M=

* Compt. Rend. **88**, 880.

molecular weight, and n==the number of atoms in the molecule. Thus dixylylmethane gave, on calculation, 36.24 atoms in the molecule and the molecular weight, 249. Theoretically, there are 37 atoms in the molecule and the molecular weight of dixylylmethane is 224. The other fractions passing over at between 308°-311° and 314°-316°, evidently must be isomers of dixylylmethane, as they would give the same molecular weight from Longenescu's formula. This may mean that some o-xylene was changed to m-xylene by aluminum chloride, which probably may account for the isomers.

It is interesting to observe the regularities in the boiling points of the homologues of diphenylmethane, which give a rule peculiar to this polycyclic group. Diphenylmethane boils at 260°-262°, ditoluylmethane at 285°-287°, dixylylmethane at 311°-313°, dimesitylmethane at 335°-337°, showing a constant rise of about 25° for each addition of two methyl groups. Kopp observed a rise of 30 degrees for each addition of a methyl group, as in the case of benzene, b. p. 80°.5, toluene, b. p. 111°, o-xylene b. p. 142° and pseudocumene b. p. 171°. This he found true, only when the methyl group entered the ring.

Density of Dixylylmethane at 25.

Pyknometer+water	=41.421
Pyknometer alone	=23.936
Weight of water	17.485
Pyknometer+dixylylmethane	=40.970
Pyknometer alone	=23.936
Weight of dixylylmethane	17.034

By the well known formula $d\ {}^{t^\circ}_{4^\circ} = \frac{W'D}{W} - \frac{.0012(W'-W)}{W}$ corrected for the buoyancy of the air, the value of density comes to be .9711.

Viscosity of Dixylymethane at 25.

	Hours	Min.	Sec.	
Water.....	= 0 ·	4	48	To run through the apparatus.
Dixylylmethane	= 1	5	50.8	

By the well known formula:

$$V = \frac{t_2 X D'}{t_1 X D}$$ the viscosity comes to be 13.35.

Tetramethylanthracene:

The distillate (c) passing over between 330°-400° could not be distilled through Liebig's condenser, as it solidified in the side-tube of the distilling flask and blocked the passage. So an air condenser was used with satisfactory results. The distillate was a yellow semi-solid, waxy in nature. This was washed over the filter paper with chloroform, when it carried away the oily substance, leaving behind yellow crystalline solid. The solid was then recrystallized from a mixture of warm benzene and alcohol several times, when the substance was obtained in a pure form. It crystallized in yellow, monoclinic plates of pearly lustre. In solution it showed an intense, green fluorescence, instead of blue or violet, as in the previous cases. The substance does not melt sharply, but decomposes at 223°-235°. It can be sublimed like other anthracenes, and the sublimed crystals show wonderful irridescence. Analysis gave:

Found C = 92.23 and H = 7.22 Calc. for $C_{18}H_{18}$ C = 92.30 and H = 7.70

The molecular weight determination by the cryoscopic method gave:

Found 219 Calc. for $C_{18}H_{18} = 234$

Friedel and Crafts* prepared a tetramethylanthracene from m-xylene with a m. p. 162°-163°, while Anschütz** obtained from m-xylene an entirely different tetramethylanthracene with m. p. of above 280°. Dewar and Jones† obtained the same tetramethylanthracene described by Anschütz, by treating m-xylene and nickel-carbonyl by aluminium chloride, which they designated as

* Ann. Chim. Phys. VI, 11, 268.
** Ann. 235, 174.
† Trans. Chem. Soc. 85, 213.

2:4:6:8 derivative. Anschütz also obtained from o-xylene a tetramethylanthracene with a m. p. of 280°, which Richter believed to be 1:3:5:7 compound.

It is evident from these facts that the compound prepared above is an isomer of the one prepared by Anschütz. The exact structure of it has not yet been determined, although from the structure of Anschütz's compound, it appears to be 2:4:6:8 derivative. There are three tetramethylanthracenes possible from o-xylene. From what has already been stated concerning these reactions, this one may be represented as analogous with those given before.

$$4C_6H_4(CH_3)_2+(CH_2O)_3+Al_2Cl_6=CH_2[C_6H_3(CH_3)_2]_2 + C_{18}H_{18}+H_2+3H_2O+Al_2Cl_6.$$

Since the preliminary part of this work was published in the Journal of American Chemical Society of July, 1914, Huston and Ewing* have worked on p-xylene and trioxymethylene in the presence of aluminum chloride, under conditions similar to those in this paper. It must be stated here that the study of p-xylene and trioxymethylene was not taken up in this laboratory for the simple reason that the formation of anthracene was not expected from it, owing to steric hindrance, although the study of it was intended to be taken up later. Contrary to all expectations, however, this work was taken up by Huston and Ewing, and as their results are interesting, the work is described below.

p-Xylene and Trioxymethylene:

To 50 grams of p-xylene 12 grams of trioxymethylene were added, and then 20 grams of aluminum chloride added piecemeal, with constant stirring. The temperature did not go beyond 60° during the reaction. Fumes of hydrochloric acid were liberated in abundance. After keeping the reaction mixture for five days at zero temperature, it was treated with ice-water and extracted with ether. A yellow precipitate was seen, which was filtered off by suction and washed with ether. This recrystallized from benzene several times, gave a pure substance, which melted at 204°-205°, with partial decomposition. The analysis gave:

Found: C=90.69, H=8.7, Calc. for $C_{35}H_{30}$

C=91.24, H=8.76

* J. Am. Chem. Soc. 37, 2394.

The molecular weight determination by the boiling point method gave 463; theoretical 460. This was designated mythylene-dis-di-p-xylylmethane.

The fluorescent ether extract was distilled, collecting the distillates (a) 306°-319°, and (b) 330°-340°. The distillate (a) redistilled passed over at 313°-316°. It solidified in long white needles, soluble in benzene, ether, chloroform and alcohol. It melted at 60-60.5. The molecular weight determination gave 231; theoretical 224. Analysis gave: Found: C=90.92, H=8.95 Calc. for $C_{17}H_{20}$, C=91.01, H=8.99. This, therefore, is di-p-xylylmethane, an isomer of the di-o-xylylmethane, described in this paper.

The distillate (b) recrystallized from a mixture of benzene and alcohol, crystallized in colorless plates. It did not show the slightest fluorescence, neither did it have anything common with anthracene derivatives. It melted at 157°-158°. Huston and Ewing believed this to be a trinucleur compound of the type of p-xylylmethyl-di-p-xylylmethane.

This partly different behavior of the reaction can be explained by means of steric hindrance that p-xylene offers for the formation of an anthracene derivative. For anthracene formation the second methylene group will have to enter in the ortho position to the first methylene group, which offers steric resistance. Hence the two methylene groups probably enter in para position to each other, and thus give rise to multi-nucleur compounds. In the case of o-xylene, however, it is quite different. The first methylene group can enter in the para position to one of the methyl groups, in preference to other positions. Thus the second methylene group also enters in the para position to the remaining methyl group, or in other words, in ortho position to the first methylene group. An anthracene derivative is made possible thereby.

It must be noted, however, that none of the previous investigators, working with CH_2Cl_2, CH_2O, methylal, or dichlortrioxymethylene, could obtain compounds similar to those obtained by Huston and Ewing. This shows that the evidence is more in favor of the reaction mentioned in this paper, than of that in the case of Huston and Ewing, although their reaction might be explained as being different, owing to steric hindrance.

Mesitylene and Trioxymethylene:

To 200 grams of mesitylene 30 grams of trioxymethylene were added at ordinary temperature. Fifty-five grams of aluminum chloride were added to it in small quantities with constant stirring. The temperature never rose above 50 degrees during the reaction. As usual hydrochloric acid gas was liberated and the color of the mixture changed to a dark red. The upper layer of the liquid showed a deep violet fluorescence. After allowing the reaction mixture to stand for two days at ordinary room temperature, it was treated with ice-water as in previous cases, and extracted with ether. No sooner was the ether added, than an amorphous substance of a yellow color was precipiated from the oily layer. It was first thought to be an aluminum compound, but was found to be entirely organic. It distributed itself between the upper layer of the ether and the lower layer of water. It was separated and washed with alcohol and recrystallized from a mixture of benzene and chloroform several times. It was not soluble in any other solvents, except benzene, chloroform and carbontetrachloride. The purified substance melted at 286°-287°. It was a light yellow crystalline powder, giving all the general charactertics of anthracene derivatives. In sulphuric acid solution it gave a deep red color, which on addition of potassium dichromate became deep green, a characteristic test for anthracene derivatives given by Dewar and Jones.* No anthracene derivative was obtained by either Dewar and Jones or by Baeyer,** in their respective work. It is evident that an anthracene derivative cannot be made directly from mesitylene. On the contrary, an anthracene derivative, either tetramethyl or hexamethyl, is not impossible indirectly. Aluminum chloride may transform part of mesitylene to pseudocumene, thus giving rise to a hexamethylanthracene, or one of the methyl groups of mesitylene may be detached from it, thus reducing it to m—xylene, which may give tetramethylanthracene. A multi-nucleur compound of the type obtained by Huston and Ewing, is also not impossible. The analysis is rather low for both anthracenes. It is equally so for the multi-nucleur compound.

* Trans. Chem. Soc. 85, 218.
** Ber. 5, 1098.

Found: C = 89.60, H = 8.45.

Calc. for $C_{18}H_{18}$. C = 92.10, H = 7.70

Calc. for $C_{20}H_{22}$. C = 91.60, H = 8.40

Calc. for $C_{39}H_{48}$. C = 90.62, H = 9.30

Unfortunately the substance was not obtained in sufficient quantities to make further analysis and molecular weight determinations.

Dimesitylmethane:

The filtered ether extract, when distilled, gave three fractions, as follows: (a) 90°-200°, (b) 200°-325°, (c) 325°-350°. At this point it showed signs of decomposition. The distillate (a) consisted of small amounts of benzene, toluene, xylene and mesitylene, together with some ether. The second distillate appeared at first as an oily liquid, but crystallized later on. The crystals had an adhering oil, from which they were separated, by washing rapidly with ether on the filter paper, whereupon the oily substance was immediately dissolved, leaving the crystals, which were less soluble. Recrystallized from a mixture of warm alcohol and ether, the purified crystals melted at 129°-130°. The crystals were white monoclinic plates. Analysis gave numbers for dimesitylmethane, a substance first prepared by Baeyer, from mesitylene, formaldehyde and sulphuric acid. Both physical and chemical characteristics checked well for dimesitylmethane.

Durene:

The fraction (c) between 325°-355° consisted of solids, together with some oil. Both the oil and the solid were extremely soluble in all the common solvents, thus offering great difficulty in separating them through crystallization. The crystals were therefore finally separated from the oil by using unglazed porcelain, which absorbed the oil. The crystals were then purified by recrystallizing from 95 per cent alcohol. The pure crystals melted at 79°-80°.

A microscopic examination proved that the crystals were different from those of dimesitylmethane. They were anisotropic, showing beautiful colors when the nicols were crossed.

They were biaxial with parallel extinction. Analysis gave:

Found: C = 90.2, H = 9.65

Calc. for $C_{10}H_{14}$; C = 89.60, H = 10.40

This did not have any characteristics of an anthracene derivative, although one of the anthracene derivatives, b-dimethylanthracene, melts at 71°. The analysis, though not so close for durene, is rather off for an anthracene derivative. It did not give an anthraquinone derivative when treated with chromic acid, but evolved carbon dioxide. Its dibromcompound melted at 199°-200°, as did that of durene. Its dinitrocompound was identical with that of durene, prepared by Anschütz, and melted at 205°-207°. There seems to be no doubt, therefore, but that this substance is durene.

That the above reaction with mesitylene is complex, is evident from the formation of benzene, toluene, xylene and durene. The formation of durene from the lower homologues was observed by Anschütz*, who first showed that all the benzene homologues were formed, more or less, from a single homologue of benzene, by the action of aluminum chloride.

Pseudocumene and Trioxymethylene:

To 210 grams of pseudocumene, 35 grams of trioxymethylene were added, and then 40 grams of aluminum chloride, added piece-meal, with constant stirring. At first aluminum chloride seemed to dissolve in the mixture, which became red in color. But later, when more aluminum chloride was added, the dissolved aluminum chloride was precipitated, and the color of the solution was changed to a bluish violet. Hydrochloric acid was liberated in large quantities. The temperature, during the reaction, was never more than 70 degrees. After the reaction mixture was kept at room temperature for three days, it was treated with ice-water. The water did not react vigorously with the reaction mixture, dissolving the aluminum chloride, as it did in other cases. Therefore, it was kept covered with water for about three days. No oil was separated, but there was a sticky, solid mass at the bottom. The water was decanted, the solid mass washed several times with fresh water, and after being dried,

* Ann. 235, 178-190.

was dissolved in a mixture of chloroform and ether in the proportion of 4:1. The solution was of red color, but when either more ether or alcohol was added, the color changed to a dark brown. If more than a required quantity of alcohol is added, a sticky substance of dark brown color is precipitated. The substance could not be precipitated as a powder, from the colloidal solution, by adding a drop or two of an electrolyte. It was found, however, that pouring the colloidal solution from one beaker into another, from a height of a little more than twelve inches, precipitated the substance in a fine powdered form, which settled down immediately. This was filtered and to the filtrate more alcohol was added, when the color of the solution changed, and the colloidal solution was the result. It was found later that methyl alcohol gave better results. The substance was precipitated by the same method in this case also. This was filtered and the filtrate was preserved for distillation. The second substance did not melt, but vaporized completely, between 130°-140°.

The substances could not be obtained in a sufficiently pure form for analysis and molecular weight determinations. The qualitative tests show, however, that the substances are hydrocarbons of the type of diphenylmethane and anthracene.

Pyridine and Trioxymethylene:

To 50 grams of pyridine 7 grams of trioxymethylene were added in a beaker, which was placed in cold water. About 40 grams of anhydrous aluminum chloride were added piece-meal. When the aluminum chloride was being added, a violent reaction, amounting to almost an explosion, took place, and white fumes of peculiar odor were liberated. No hydrochloric acid gas was liberated during the reaction, showing that it was being absorbed by the reacting mixtures. A white solid was at first precipitated, but when more aluminum chloride was added, the white precipitate was redissolved and the color of the product changed to dark red, becoming viscous at the same time. When the required quantity of aluminum chloride had been added, the mass became sticky and almost solidified. It was kept at room temperature for almost a year.

When water was added to the reacting mixture, it did not show any action on the product, but dissolved all the material.

It was also soluble in alcohol, producing a reddish brown solution. When evaporated, this solution gave a reddish brown substance, crystallizing in radiating needles. It contained some aluminum. The water solution, after being filtered, was distilled at ordinary pressure. Part of the substance passed over at below 100°, and was mostly water with some pyridine. The temperature then suddenly rose to 200° and a white crystalline substance, together with a red oil, began to distill, until 260° was reached. The white crystals were separated from the oil and recrystallized from alcohol. The purified crystals melted at 76°-77°. They were white needles and were soluble in water, alcohol and acetone, but were insoluble in ether, benzene and chloroform. They contained chlorine, as indicated by the flame test.

On redistilling, much of the crystalline substance decomposed, consequently yielding very little of the pure material. A very large quantity of the red oil, was obtained, which had a penetrating odor. The crystalline substance, being insufficient for analysis, was converted into a salt of platinum chloride, which melted at 130°-131°. The platinum determination was, however, made.

pt crucible+substance	=32.380
pt crucible only	=32.349
substance	.031

Heated on a blow pipe:

pt crucible+substance	=32.355
pt crucible only	=32.349
the platinum	.006

This gives 19.6 per cent platinum in the salt.

A number of chlor and hydrochlor pyridines are known, but none of them seem to be identical with the crystalline substance mentioned above. The following is a comparision of the known substances with the crystalline substance prepared in this laboratory:

Known Compounds of Pyridine.

$C_5H_5NCl.HCl$ is insoluble in water.

$C_5H_3Cl_2N.HCl$ melts at 72°, boils at 130°, gives a yellow salt of $(C_5H_3Cl_2N.HCl)_2PtCl_4$ with 27% of Pt.

$C_5H_3Cl_2N$ melts at 87°-88°, boils at 200°-220°, is insoluble in water.

$C_5H_2Cl_3N$ melts at 71°-72°, boils at 200°, is insoluble in warm alcohol.

$(C_5H_5NHCl)_2PtCl_4$ is red, melts at 240°, is soluble in water but not in alcohol, has 34% Pt.

$(C_5H_5NCl_2)_2PtCl_4$ melts at 204°, has 30% Pt.

New Substance:

Pyridine salt melts at 77°, boils at 200°-22°, is soluble in alcohol, water and acetone, gives a yellow salt of $PtCl_4$, which melts at 130°, soluble in water and alcohol, and has 19.6% of Pt.

Formaneck* obtained a compound $C_5H_5NH_2CO$ from pyridine and formaldehyde after heating them for several hours. But it must be noted that the percentage of platinum does not agree with a compound of this type, nor with those already mentioned above. The results agree better with compounds of the type of dyphenylmethane and anthracene. A compound like $CH_2(C_5H_4ClNHCl)_2.PtCl_4$ has 20.0 per cent of platinum while a compound like

$$(C_5H_3ClN.HCl<\begin{matrix}CH_2\\CH_2\end{matrix}>C_5H_3ClN.HCl)_2PtCl_4$$

has 19.70 per cent of platinum.

In result, at least, the crystalline substance resembles more a compound of the anthracene type than the type of diphenylmethane. The red penetrating oil, therefore, must be a compound of the type of diphenylmethane.

Hexane and Trioxymethylene:

To a mixture of 300 c.c. of hexane and 40 grams of trioxymethylene, 175 grams of anhydrous aluminum chloride were added, piece-meal, with constant stirring. The reaction was not vigorous as in other cases, but was very slow, although hydrochloric acid gas began to be liberated soon after the first few grams of aluminum chloride were added. After a few hours the product changed to a dark red solid cake. Most of the unchanged hexane evaporated. The reaction mixture was kept for

* Ber. 38, 944.

about a month at room temperature, after which time, it was treated with ice-water. Thick white fumes began to be liberated as soon as the temperature arose beyond a certain point. When decomposed by water, the product separated into two layers, one of water, and the other of oil. The oil was a dark liquid, with a terpinelike odor, which solidified, when exposed for a time. This solid was resinous and was transparent. It was dissolved in ether and the ether solution was subjected to vacuum distillation.

At 50 m.m. pressure a yellow oil passed over, between 140°-220°. Between 220°-255° a greenish yellow oil distilled over, which solidified to a resinlike substance, and had the odor of a terpine. The yield, however, was too small for further investigation. It is interesting to note in this connection, that there was a distinct reaction between hexane and trioxymethylene, although Nastukoff* asserted that there was no reaction between hexane and trioxymethylene in the presence of aluminum chloride. After the preliminary work on trioxymethylene was published in the Journal of the American Chemical Society, vol. 36, 1529-1537, A. M. Nastukoff and Gurin worked on trioxymethylene and some aliphatic hydrocarbons in the presence of aluminum chloride. By working with cyclo-hexane and trioxymethylene in the presence of aluminum chloride, they obtained (1) hexamethylbenzol, (2) an unidentified compound, probably dodecanaphtene, or hydrogenated diphenylmethane, or dicyclohexyl, (3) formolith. In their conclusions, they assert that heptane and octane enter into the reaction, while pentane and hexane do not. They further state that aluminum chloride does not react alone on pentane, hexane, heptane, octane and cyclohexane, forming addition products, which clearly proves, they say, that their reaction is different from that of Gustavson. It may be interesting to note that quite contrary results were obtained in this laboratory. The hexane used in the reaction was Kahlbaum's preparation from petroleum. It was found that hexane and octane reacted with trioxymethylene much more easily than pentane, and heptane.

Benzene and Formaldehyde:

The reaction of trioxymethylene in the presence of alumi-

* J. Russ. Chem. Soc. 47, 46-52.

num chloride, though identical with Baeyer's reaction in many respects, appeared to differ slightly with the reaction of formaldehyde in the presence of sulphuric acid. Baeyer obtained anthracene by the action of formaldehyde on diphenylmethane, while the same compound could not be obtained in this laboratory by the action of trioxymethylene on diphenylmethane. Trioxymethylene is known to have quite different properties from formaldehyde. Such facts as these suggested the experiments with formaldehyde. Five experiments were made with formaldehyde and benzene in the presence of aluminum chloride. In one instance formaldehyde was made by heating trioxymethylene, but as it polymerized immediately in the delivery tube, and exploded once, it was thought better to produce the gas by some other method. In other cases formaldehyde was produced by heating 40 per cent formaline and drying it with sulphuric acid. 100 c. c. of benzene were mixed with 5 grams of aluminum chloride in each experiment, and dried formaldehyde gas was passed through it slowly. In the first experiment, the gas was passed through for one hour, at a temperature of 18°-20°. In the second, it was passed for two hours at the same temperature. In the third, it was passed for about three to four hours, until the solution was almost saturated with formaldehyde. The temperature arose once to 42° during the experiment. The product became quite viscous, at times solidifying in the delivery tube, thus blocking the passage of the gas. In the fourth, the gas was passed for two hours, at a temperature of 45°-55°.

In each case the reaction product was treated with ice-water and the separating oil was extracted with ether. The ether extract was then subjected to distillation. In all the experiments, the extract had a green fluorescence. In one case, only, out of the four experiments, a good yield was obtained. In other cases, the reaction did not seem to be completed. In the third experiment the fractions were collected as follows: (a) 60°-120°, (b) 256°-280°. There remained after the distillation, a tarry substance. The fraction (a) consisted of ether, benzene and probably some toluene. After the first fraction was distilled, the temperature suddenly rose to 256°, and an oil, mixed with a waxy solid, began to distill, until a temperature of 280° was reached. The oil, after being separated from the solid, was re-

distilled, when it passed over at 259°-262°. It was identified as being diphenylmethane from its chemical and physical properties. The solid, when dissolved in benzene, showed a blue fluorescence, and crystallized from it in pearly scales, melting at 211°-213°. It gave anthraquinone and showed all the characteristics of anthracene. This shows that formaldehyde and trioxymethlene act alike on benzene in the presence of aluminum chloride, forming diphenylmethane and anthracene.

The Reaction:

The role of aluminum chloride in the above experiments has been a matter of much speculation. The fact that hydrochloric acid is evolved in both the Friedel and Crafts' reaction and in the "New Phase" has caused confusion. But a little thought will show that this "New Phase" of catalysis is entirely different. Hydrochloric acid is evolved as a primary by-product in the Friedel and Crafts' reaction. It is formed from the halogen of the halide and the hydrogen of the aromatic compound. In the "New Phase," however, it is formed as a secondary by-product. Neither benzene nor trioxymethylene has any chlorine, and hence the evolution of hydrochloric acid cannot be the result of the catalytic power of aluminum chloride. It can only be explained by presupposing the dehydrating power of aluminum chloride, which when acted on by water, liberates hydrochloric acid. The primary role of aluminum chloride in this reaction, therefore, is dehydration. Hydrochloric acid, itself, has been known as a dehydrating agent, and has been used as such, in the synthesis of glucosides, by Emil Fischer, and in the condensation of formaldehyde and salicylic acid by Madsen, as has been mentioned before. It is evident that hydrochloric acid, though a dehydrating agent, cannot be the cause of the reaction. It is not found to react with benzene and trioxymethylene, under conditions under which aluminum chloride acts on them. It is necessary to digest it in the reacting mixture at a high temperature. Besides it is a secondary by-product, and if the reaction can be explained by aluminum chloride alone, it is unreasonable to take it into account. It is interesting to note that the gases evolved in the reaction of benzene and trioxymethylene in the presence of aluminum chloride, if passed

through an identical mixture, under identical conditions, do not bring about the reaction, of the second reacting mixture. On the other hand, chlorine cannot be supposed to have brought about the reaction. Aluminum chloride acts as a dehydrating agent almost universally, and even in the familiar test of ethylacetate from alcohol and acetic acid, it can be used instead of sulphuric acid. Thus it can be said beyond a doubt, that the reaction of aluminum chloride is primarily due to dehydration and not to any other cause.

Summary:

1. It has been shown in this paper that trioxymethylene, by reacting on hydrocarbons, in the presence of aluminum chloride, gives condensation products similar to those obtained by Baeyer, by the action of formaldehyde on hydrocarbons, in the presence of sulphuric acid. Thus compounds of the type of diphenylmethane and anthracene are invariably obtained as condensation products. It has also been shown that trioxymethylene does not give anthracene by its action on diphenylmethane, as does formaldehyde.

2. That formaldehyde acts similar to trioxymethylene on hydrocarbons in the presence of aluminum chloride.

3. That aluminum chloride detaches the methyl groups from mesitylene, transplanting them back again in other positions, thus giving rise to durene and m-xylene.

4. That aluminum chloride has the power of transporting chlorine atoms, as in the case of a pyridine compound.

5. That hexane and trioxymethylene react, giving terpine-like compounds, contrary to the assertions of Nastukoff and Gurin.

6. That the reaction of aluminum chloride is primarly due to its dehydrating power and to nothing else.

BIOGRAPHICAL SKETCH.

Mr. Vaman R. Kokatnur was born in a small town in the Bombay Presidency, India. He went to the grammar school in the same town and later entered the "New English High School" of the Deccan Education Society in Poona City, India. After graduating from that high school in 1906, he entered the Fergusson College of the Deccan Education Society in the same city. In 1911 he joined the Wilson College in Bombay and took the B.Sc. degree from the Bombay University in 1912, specializing in chemistry and geology. He served as a chemist at the Ranade Industrial and Economic Institute for about six months until he came to this country and entered in the graduate school of the University of California at Berkeley, Cal., during 1912-1913. After a year's study in California, he came to the University of Minnesota and entered the graduate school in the year 1913-1914. In June, 1914, he took M. S. majoring in chemistry and minoring in geology. During the year 1914-1915 he was appointed to "Shevlin Fellowship" in chemistry. He was elected to membership in Sigma Xi in 1914, after taking his M. S. In 1915-1916 he was appointed Research Assistant to Dr. G. B. Frankforter. In June, 1916, he took the degree of doctor of philosophy in chemistry and geology.